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TITLE Structural Distortion in R Platinum₂ Tin₂ Compounds (R= Rare Earths)

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SUBMITTED TO To be presented at the 10th International Conference on Solid Compounds of Transition Elements, May 21-25, 1991 Munster, W. Germany

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STRUCTURAL DISTORTION IN $R\text{Pt}_2\text{Sn}_2$ COMPOUNDS (R - RARE EARTH)

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Full paper contributed to the Proceedings of the 10th International Conference on Solid Compounds of Transition Elements, May 21-25, 1991, Munster, West Germany

Submitted May 8, 1991

LA-UR-91-

CeM_2X_2 compounds (M-transition metals, X = Si, Ge, Sn) exhibit very exotic properties such as intermediate valence state, heavy fermion, magnetism, and superconductivity. Most of them crystallize in the ThCr_2Si_2 type structure (14/nmm) while a few adopt the CeBe_2Ge_2 primitive one (P4/nmm). Among these compounds, CePt_2Sn_2 has the heaviest known specific heat coefficient ($\gamma = 3.5 \text{ J/mol}\cdot\text{K}^2$) and orders antiferromagnetically at $T_N = 0.88 \text{ K}$.

Samples of CePt_2Sn_2 , $\text{Ce}_{0.6}\text{La}_{0.2}\text{Pt}_2\text{Sn}_2$, and LaPt_2Sn_2 have been studied by X-ray powder diffraction experiments including Rietveld calculations before and after annealing. As-cast samples can be indexed in the tetragonal primitive cell; however, re-examination of annealed samples (1 & 3 days at 800°C and 3 weeks at 700°C) reveals a monoclinic distortion of the lattice. Such a distortion has already been observed for CeNi_2Sn_2 .

Furthermore, our diffraction patterns show evidence for superlattice lines at twice the unit cell parameters, which was verified by transmission electron microscopy. Microprobes analysis on these samples show that the Pt sublattice is slightly substoichiometric (97.5%). Thus strains due to large atomic radii and ordering of Pt vacancies could be responsible for the monoclinic distortion and superlattice lines.

STRUCTURAL DISTORTION IN $R\text{Pt}_2\text{Sn}_2$ COMPOUNDS (R - RARE EARTHS)

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ABSTRACT

Most of the RM_2X_2 compounds can be described in tetragonal systems either in the ThCr_2Si_2 type or in the CaBe_2Ge_2 one. However, recent works have shown that for large size atoms such as Pt or Ir for M and Ge or Sn for X, structural distortions occur leading to less symmetrical cells. Here, we report on $\text{Ce}_x\text{La}_{1-x}\text{Pt}_2\text{Sn}_2$ ($x = 1, 0.8$ and 0) compounds which exhibit monoclinic distortion and superlattice lines after annealing.

INTRODUCTION

RM_2X_2 compounds (R=Rare Earths, M=Transition Metals and X=Si, Ge or Sn) exhibit very exotic physical phenomena: Kondo lattice effects, heavy fermion behavior, superconductivity in heavy fermion state, charge and valence fluctuations...[1]. Most of these compounds adopt the tetragonal ThCr_2Si_2 [2] structure which is derived from the BaAl_4 one [3] where Al1 and Al2 atom sites are filled up by M and X atoms respectively. In this structure, direct contact between M atoms is avoided and it should be pointed out that it is a general feature for these compounds. Even in the case of CeZn_2Al_2 [4] which crystallized in the anti- ThCr_2Si_2 where M and X sites are exchanged allowing direct contact between Zn atoms, the metal distances are still metallic ones. A few compounds [5,6] are reported to crystallize in the CaBe_2Ge_2 type structure [7] which can be described as a stacking along c axis of half slab of ThCr_2Si_2 type and half slab of anti- ThCr_2Si_2 . Among them, CePt_2Sn_2 which exhibits the heaviest known electronic specific heat coefficient [8], has been first reported in a tetragonal cell ($a=4.581 \text{ \AA}$, $c=10.385 \text{ \AA}$) [9]. Here we report evidence for a monoclinic distortion observed after annealing for $\text{Ce}_x\text{La}_{1-x}\text{Pt}_2\text{Sn}_2$ ($x=1, 0.8$ and 0) compounds. Furthermore, profile calculations and electron microscopy show superlattice lines leading to twice the unit cell parameters for CePt_2Sn_2 . This structural behavior will be discussed with regard to Pt vacancies and/or to strain effects due to large atomic sizes.

EXPERIMENTAL DETAILS

The three samples have been prepared by arc melting of the constituents, Ce or La (99.9%), Pt (99.99%) and Sn (99.999%) on a water cooled copper hearth in an argon atmosphere. Each sample was melted five times in order to insure homogeneity. To check the influence of annealing treatments on the structural properties, the samples have been annealed one and three days at 800°C and three weeks at 700°C in a quartz tube sealed under vacuum.

Metallographic examinations confirmed the samples to be single phases. Microprobe analyses show that the samples are stoichiometric though a slight substoichiometry effect ($\approx 2.5\%$) for Pt is systematically observed.

X-ray powder diffraction experiment have been carried out on a Philips step by step goniometer using $\text{CuK}\alpha$ radiation (1.54178 \AA). Profile refinements have been calculated using RIETVELD method. Electron microscopy have been performed on a JEOL 2000FX transmission microscope.

L_{III} absorption edge measurements, which have been performed previously, have shown that the Ce ion is in the trivalent state for CePt_2Sn_2 [10] and have been also checked for the substituted compound.

RESULTS AND DISCUSSION

X-ray diffraction powder patterns of as cast samples can be indexed in the primitive tetragonal cell (space group $P4/nmm$) of the CaBe_2Ge_2 type structure as expected from previous structural studies reported on a single crystal of CePt_2Sn_2 [9]. However, powder pattern examinations of annealed samples show evidence of a structural distortion and have been indexed in a monoclinic cell (see Table I). A systematic study of annealing effects has shown that the distortion occurs whatever the treatment conditions are: 1 or 3 days at 800°C or 3 weeks at 700°C . In fact, accurate examination of the as cast sample patterns shows that the monoclinic distortion can be expected if one considers the presence of shouldering in some of the main peaks. Then, the tetragonal structure of the as cast samples can be seen as a metastable state which transforms itself to the monoclinic one when annealed. Such a distortion has been already reported for CeNi_2Sn_2 for which the authors [11] observed a splitting of some X-ray diffraction lines when annealing the sample at 700°C for one week. However they report that annealing at 800°C do not lead to any distortion. More recently, the structural study of EuCu_2Sn_2 have shown that this latter compound crystallizes in a monoclinic cell ($a=4.823 \text{ \AA}$, $b=4.308 \text{ \AA}$, $c=10.566 \text{ \AA}$ and $\beta=96.6^\circ$) [12] and its structure can be described as a strongly distorted

ThCr_2Si_2 one. Monoclinic distortion of the CaBe_2Ge_2 structure have been also already reported for LaPt_2Ge_2 [13] where the authors proposed to describe this compound in the monoclinic space group $P2_1$. Then, we attempt to refine CePt_2Sn_2 and LaPt_2Sn_2 in such a structural description using the Rietveld refinement method. Final cycles lead to R factors of 11.5% for Ce and 11.9% for La compounds which corresponds to a rather poor fit. Furthermore, diffraction patterns show evidence for superlattice lines (figure 1) which can not be indexed even in this monoclinic cell but which can be taken into account when doubling the cell parameters. Careful study have been made in order to check the possibility of the emergence of a second phase during annealing responsible of such diffraction lines but neither metallographic examinations nor microprobe analyses on both as cast and annealed samples confirm this hypothesis. Thus, electron transmission microscopy experiments were undertaken to check the validity of a double cell. Figure 2 shows the diffraction planes $(2-2\ 1)^*$ and $(-3\ 0\ 1)^*$ of CePt_2Sn_2 and the presence of weak extra spots between the main Bragg spots of the simple monoclinic cell confirms the existence of the superlattice. At this stage, we have tried to refine X-ray powder patterns in a double cell but difficulties to handle such a large cell size and to describe correctly atomic positions have not lead yet to reliable results.

CONCLUSION

Most of the MX_2X_2 compounds can be described in tetragonal system either in the ThCr_2Si_2 type or in the CaBe_2Ge_2 one. However, recent works have shown that upon substitution, when increasing the size of M or X (i.e. $\text{M}=\text{Ir}$ or Pt , $\text{X}=\text{Ge}$ or Sn), structural distortion occurs leading to less symmetrical cells. In first approximation, this could be understood as a geometrical effects. Moreover, analyses reveal a systematic substoichiometry for M atom sublattice and thus strains due to large atomic radius sizes and ordering of M vacancies could be responsible for monoclinic distortion as well as for superlattice lines in CePt_2Sn_2 . It should be pointed out that this latter compound has the heaviest known specific heat coefficient ($\gamma=3.5\text{ J/mol.K}$) and

then particular attention must be paid in future studies to the relation between structural distortion and physical properties.

FIGURE CAPTION

Figure 1: X-ray powder diffraction patterns for a) CePt_2Sn_2 b) LaPt_2Sn_2 (.... experimental pattern, — calculated pattern, + peak positions). The difference curve between calculated and experimental patterns appears below at the same scale. Superlattice lines are shown by arrows.

Figure 2: Diffraction planes a) $(2 -2 1)^*$ b) $(-3 0 1)^*$ for CePt_2Sn_2 .

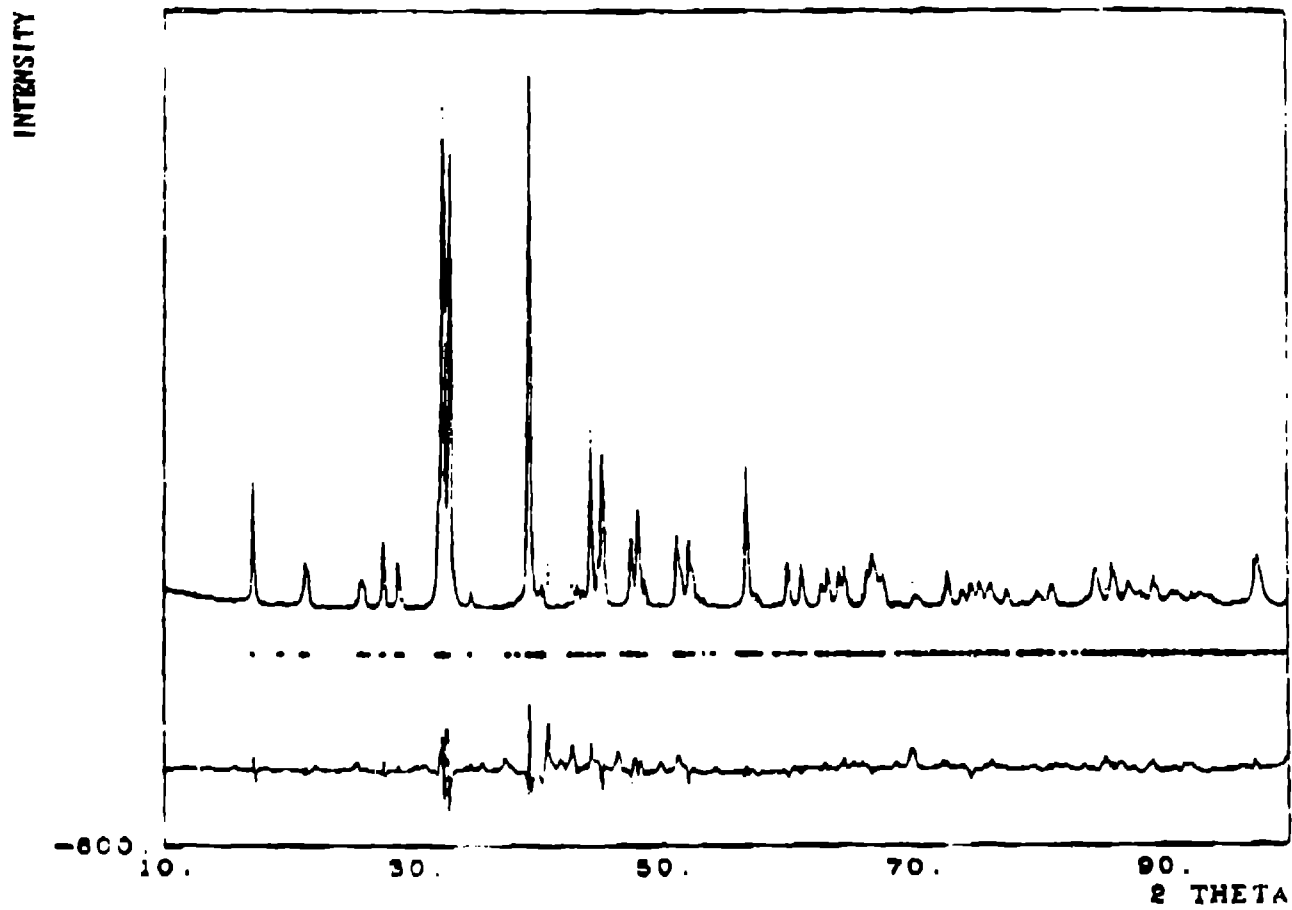
REFERENCES

- [1] L.C. Gupta and S.K. Malik (eds.), *Valence Fluctuations and Heavy Fermions*, Plenum, New York, 1987.
- [2] Z. Ban and M. Sikirica, *Acta Cryst.*, **18** (1965) 594.
- [3] A. Andres and Albertini, *Z. Metallk.*, **27** (1935) 126.
- [4] G. Cordier, B. Czeh, H. Schafer and P. Woll, *J. Less Comm. Met.*, **110** (1985) 327.
- [5] R.V. Skolozdra and L.P. Komarovskaya, *Ukr. Fiz. Zh.*, **27** (1982) 1834.
- [6] A. Dommann, F. Mulliger and R. H. Ott, *J. Less-Common Met.*, **110** (1985) 331.
- [7] B. Eisenmann, W. May, W. Muller and H. Schafer, *Z. Naturforsch.*, **B27** (1972) 1155.
- [8] W.P. Beyermann, M.F. Hundley, P.C. Canfield, J.D. Thompson, M. Latroche, C. Godart, M. Selsane, Z. Fisk and J.L. Smith, *Physical Review B*, submitted in 1990.
- [9] M. Selsane, M. Lebaill, N. Hamdaoui, J.P. Kappler, H. Noel, J.C. Achard and C. Godart, *Physica B*, **163** (1990) 213.
- [10] M. Selsane, J.C. Achard, C. Godart, W.P. Beyermann, M.F. Hundley, P.C. Canfield, J.L. Smith, J.D. Thompson, N. Hamdaoui and J.P. Kappler, *Eur. J. Solid State Inorg. Chem.*, **28** (1991) 567.
- [11] T. Takabatake, F. Teshima, H. Fujii, S. Nishigori, T. Suzuki, T. Fujita, Y. Yamaguchi and J. Sakurai, *Yamada Conf. on Magnetic Phase Transition, April 13-16 1990, Osaka, Japan*, to be published in *J. Mag. Mag. Mat.*
- [12] C. Mazumdar, C. Godart, M. Latroche, R. Nagarayan, L.C. Gupta, B.D. Padalia and R. Vijayaraghavan, *Int. Conf. Mag.*, **2-6 sept 1991, U.K., Edinburgh.**

[13] G. Venturini, B. Malaman and B. Roques,
J. Less Comb. Met., 146 (1989) 271.

Parameters	CePt ₂ Sn ₂	Ce _{0.9} La _{0.1} Pt ₂ Sn ₂	LaPt ₂ Sn ₂
a (Å)	4.593(5)	4.608(5)	4.615(5)
b (Å)	4.590(5)	4.603(5)	4.610(5)
c (Å)	10.404(7)	10.412(7)	10.436(7)
β (°)	91.6(1)	91.8(1)	91.6(1)

Table 1 - Cell parameters for (Ce,La)Pt₂Sn₂ compounds



La₂Se₃

